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P. Haygarth, B.L. Turner, A. Fraser, S. Jarvis, T. Harrod, D. Nash, D. Halliwell, T. Page, K. Beven

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Temporal variability in phosphorus transfers: classifying concentration–discharge event dynamics

Phil Haygarth[1], Benjamin L. Turner[1,5], Andy Fraser[2], Steve Jarvis[1], Tim Harrod[2], David Nash[3], David Halliwell[3], Trevor Page[4] and Keith Beven[4]

[1]Institute of Grassland and Environmental Research, North Wyke Research Station, Okehampton, Devon, EX20 2SB, UK
[2]National Soil Resources Institute, North Wyke Research Station, Okehampton, Devon, EX20 2SB, UK
[3]Agriculture Victoria, RMB 2460, Hazeldean Road, Ellinbank, Victoria 3821, Australia
[4]Environmental Science Department, University of Lancaster, Lancaster LA1 4YQ, UK
[5]Soil and Water Science Department, University of Florida, Gainesville, Florida 32611, USA

E-mail for corresponding author: phil.haygarth@bbsrc.ac.uk

Abstract

The importance of *temporal* variability in relationships between phosphorus (P) concentration (C_p) and discharge (Q) is linked to a simple means of classifying the circumstances of C_p–Q relationships in terms of functional types of response. New experimental data at the upstream interface of grassland soil and catchment systems at a range of scales (lysimeters to headwaters) in England and Australia are used to demonstrate the potential of such an approach. Three types of event are defined as Types 1–3, depending on whether the relative change in Q exceeds the relative change in C_p (Type 1), whether C_p and Q are positively inter-related (Type 2) and whether C_p varies yet Q is unchanged (Type 3). The classification helps to characterise circumstances that can be explained mechanistically in relation to (i) the scale of the study (with a tendency towards Type 1 in small scale lysimeters), (ii) the form of P with a tendency for Type 1 for soluble (i.e., <0.45 μm P forms) and (iii) the sources of P with Type 3 dominant where P availability overrides transport controls. This simple framework provides a basis for development of a more complex and quantitative classification of C_p–Q relationships that can be developed further to contribute to future models of P transfer and delivery from slope to stream. Studies that evaluate the *temporal* dynamics of the transfer of P are currently grossly under-represented in comparison with models based on *static/spatial* factors.

Keywords: phosphorus, concentration, discharge, lysimeters, temporal dynamics, overland flow

Introduction

The models currently dominant for understanding phosphorus (P) transfer from agricultural soils to streams (Haygarth and Jarvis, 1999; Heathwaite *et al*., 2003; Lemunyon and Gilbert, 1993) are focused on *static/spatial* factors, such as farm system (Haygarth *et al*., 1998b), land use type (Johnes and Butterfield, 2002) and soil P status (Heckrath *et al*., 1995). In this paper, the importance of *temporal* variability is explored and it is shown that such 'day to day' changes in P concentration (C_p) – discharge (Q) relationships can be at least as important as *static/spatial* factors.

Nutrient concentration–Q relationships are well established, particularly within the engineering/hydrology disciplines using methods such as hydrograph separation and mixing models (e.g. Leaney *et al*., 1993; McDonnell *et al*., 1991). However, among the P transfer cognoscenti and in the emergent literature, there are relatively few such C_p–Q studies that involve P specifically even though P dynamics are critical to farming practices (see Table 1 and below for a review of key work). This note examines the importance of these temporal concepts in relation to P transfer and presents a simple empirical attempt to characterise C_p–Q relationships. The paper involves:

1. examination of the theoretical background as to why C_p–Q relationship types differ;
2. a proposed classification for C_p–Q relationship types;
3. a description of the methods behind the new data;
4. a discussion of how understanding C_p–Q relationships

Table 1. A selective review giving examples of phosphorus concentration–discharge circumstances published by previous researchers

Source Circumstances	*Discharge Circumstances*	*Concentration–discharge relationship*	*Reference*
Springtime manure additions – 200 tonnes ha^{-1} (New York, USA)	1319 mm annual rainfall, 'high spring discharge'. Integration of spring and summer discharge peak events	High concentration of RP and UP <0.45 μm. Some rise with discharge.	Hergert *et al.*, 1981. *J. Environ. Qual.*, **10**, 345–349.
Springtime manure additions – 35 tonnes ha^{-1} (New York, USA)	1319 mm annual rainfall, 'high spring discharge'. Integration of spring and summer discharge peak events	High concentration of RP and UP <0.45 μm. Not clearly related to discharge.	Hergert *et al.*, 1981. *J. Environ. Qual.*, **10**, 345–349.
Springtime manure additions – 200 tonnes ha^{-1} (New York, USA)	1319 mm annual rainfall, 'high spring discharge'. Integration of spring and summer discharge peak events	'Reduced' concentration of RP and UP <0.45 μm and UP in the autumn after a spring addition. No relationship between discharge and concentration.	Hergert *et al.*, 1981. *J. Environ. Qual.*, **10**, 345–349.
Springtime manure additions – 35 tonnes ha^{-1} (New York, USA)	1319 mm annual rainfall, 'high spring discharge'. Integration of spring and summer discharge peak events	'Reduced' concentration of RP and UP <0.45 μm and UP in the autumn after a spring addition. No relationship between discharge and concentration.	Hergert *et al.*, 1981. *J. Environ. Qual.*, **10**, 345–349.
Springtime manure additions – 200 tonnes ha^{-1}(New York, USA)	Irrigation experiment in the Autumn with 640 ml + 430 ml + 530 ml applied in successive days	RP <0.45 μm (90% of the TP <0.45 μm) dramatically rose in relation to increases in discharge.	Hergert *et al.*, 1981. *J. Environ. Qual.*, **10**, 345–349.
Grazed grassland 1 ha plots, after fertiliser additions, England	1100 mm annual rainfall, 50 mm rainfall over four days May 1994 six days after addition of 16 kg triplesuperphosphate fertilizer, single discharge peak event	Total P responded to the discharge hydrograph, RP<0.45 μm was unaffected.	Haygarth and Jarvis, 1997. *Wat Res.,* **31**, 140–148.
Grazed grassland 1 ha plots, after fertiliser additions, England	1100 mm annual rainfall, 140 samples of discharge and concentration (from integration of 10 occasions × 14 plots) during spring and autumn discharges from 1 ha plots during 1994. Excluded 'high' discharge events.	Relationship between RP<0.45 μm and discharge was not significant. Relationship between TP and discharge was significant but only explained 14% of the variation.	Haygarth and Jarvis, 1997. *Water Res.,* **31**, 140–148.
Permanent grassland, Lake Sempach, Switzerland	1200 mm annual rainfall, only selecting individual single discharge peak events	Positive correlation between concentration of RP<0.45 μm and discharge for 27/30 peaks and 64–79% of variance between concentration and discharge explained in linear regressions.	Stamm *et al.,* 1998, *J. Environ. Qual.,* **27,** 515–522.
Permanent grassland, Lake Sempach, Switzerland	1200 mm annual rainfall, all events (data plotted in log scale)	20–34% of variance between concentration and discharge explained in linear regressions.	Stamm *et al.,* 1998, *J. Environ. Qual.,* **27,** 515–522.
Permanent grassland, Lake Sempach, Switzerland, after manure additions	1200 mm annual rainfall, individual single discharge peak event	Fresh manure strongly affected RP<0.45 μm concentrations 1–2 days after application but not on a longer term time scale	Stamm *et al.,* 1998, *J. Environ. Qual.,* **27,** 515–522.
Cut grassland, 30 m^2 plots	Annual rainfall 1100 mm, this event 49 mm rainfall in 169 hours, intensity 0.2–3 mm h^{-1}	Pronounced storm discharge hydrograph but TP concentration remained relatively unchanged throughout.	Preedy *et al*., 2001, *J. Environ. Qual*., **30**, 2105–2112
Cut grassland 30 m^2 plots, P fertiliser added equivalent to 29 kg TP ha^{-1}	Annual rainfall 1100 mm, this event 49 mm rainfall in 169 hours, intensity 0.2–3 mm h^{-1}	Pronounced storm discharge hydrograph with corresponding rise in TP concentration.	Preedy *et al.,* 2001, *J. Environ. Qual*., **30**, 2105–2112
Cut grassland 30 m^2 plots, cattle slurry added equivalent to 29 kg TP ha^{-1}	Annual rainfall 1100 mm, this event 49 mm rainfall in 169 hours, intensity 0.2–3 mm h^{-1}	Pronounced storm discharge hydrograph with corresponding rise in TP concentration.	Preedy *et al.,* 2001, *J. Environ. Qual*., **30**, 2105–2112

can contribute to new understandings of P transfer dynamics.

Theoretical background

Phosphorus concentration and Q relationships have been discussed previously by a limited number of researchers (e.g. Cooke, 1988; Haygarth and Jarvis, 1997; Hergert *et al*., 1981a; Hergert *et al*., 1981b; Pionke *et al*., 1993; Preedy *et al*., 2001; Sinaj *et al*., 2002; Stamm *et al*., 1998). Table 1 presents a summary of these. From the literature, three types of C_p–Q response can be identified.

In Type 1, C_p remains relatively constant in relation to Q. This might arise from a steady-state situation between the dissolution kinetics of a relatively homogenous soil and the velocity of the water flow and where the reservoir of the soil water may not drain too quickly to prevent exchange of P between soil and solution. The theoretical extreme of this could be homogenised sand.

In Type 2, C_p and Q seem to be related, when the presence of fast flow causes an apparent disequilibrium in the C_p supply. In theory, this may arise when:

1. Flow causes the physical entrainment of particulate and colloidal matter (with P attached) during rapid water flows (Haygarth and Jarvis, 1997; Haygarth *et al*., 1997). This is probably the commonest example.
2. The fast flow means that the water takes a pathway different from that 'normally' experienced during saturated base flow, where there is little opportunity for mixing and re-adsorption of P. This may be exacerbated in circumstances where the fast flow path interacts with a 'new' high P source. Indeed, Haygarth *et al.* (1998a) have shown that where soil P is concentrated in the top few cm of soil, it provides a source with a high potential for interacting with any fast overland or near-surface flows. Macropore flow has also been shown to be important in these circumstances (Stamm *et al*., 1998).
3. The changes in soil moisture affect soil biochemistry and additional P is supplied. Recent studies have shown that dynamics of soil wetting and drying may release a considerable quantity of P into soil solution including mobile P from the soil microbial biomass (Turner and Haygarth, 2001).
4. A decline of C_p in relation to high Q, reflects dilution and depletion of source.

Type 3 is the opposite of Type 1, where changes in C_p occur even though Q remains relatively constant. This reflects an enriched supply or source of P to the system and could occur when fertiliser or manure is added to soil (Haygarth and Jarvis, 1997; Hergert *et al*., 1981a; Hergert *et al*., 1981b; Pionke *et al*., 1993; Preedy *et al*., 2001; Stamm *et al*., 1998).

Proposed classification for C_p–Q relationship types

Based upon the theoretical background, the C_p–Q relationships can be classified in terms of a simple decision tree (Fig. 1).

1. Define the duration (i.e. start and endpoint) of the time series to be classified, e.g. a storm, three storms, rising limb, falling limb etc..
2. Determine whether there is a significant change in C_p or Q during the time series i.e. is there an 'event' to be classified?
3. Is the event characterised by a change in C_p and/or Q?
   - Type 1 events occur when the relative change in Q is > than the relative change in C_p.
   - If both C_p and Q change then the event is Type 2.
   - If C_p only changes then the event is Type 3.

Data collected to test the classification for C_p–Q relationship types

The classification was tested on new data, derived from analysis of hydrographs and time series data for P export from a range of hydrologically isolated 'lysimeters' and headwater catchments from different soils of varying P content, for a variety of rainfall–runoff conditions in England and Australia. All samples were collected, prepared and analysed for either reactive P that was filtered (<0.45 µm, $RP_{<0.45\ \mu m}$) (Haygarth *et al*., 1995; Haygarth and Sharpley, 2000) or total P that was unfiltered (TP), using standard protocols (Eisenreich *et al*., 1975; Murphy and Riley, 1962; Rowland and Haygarth, 1997). A full description of all the sites used follows below (Table 2 summarises soil type, P status, P management and hydro-sampling methods):

Monolith lysimeters. Cylindrical monolith lysimeters, 135 cm deep and 80 cm diameter, sampled intact to preserve the soil structure (Belford, 1979) were installed in a field site (UK national mapping grid reference NGR SX 657 983) at North Wyke Research Station, Devon, UK, in 1992. The lysimeters supported swards that were dominated by perennial ryegrass (*Lolium perenne* L.) and received inorganic fertiliser nitrogen (N), P and potassium (K), in accordance with recommended practice for cut grassland

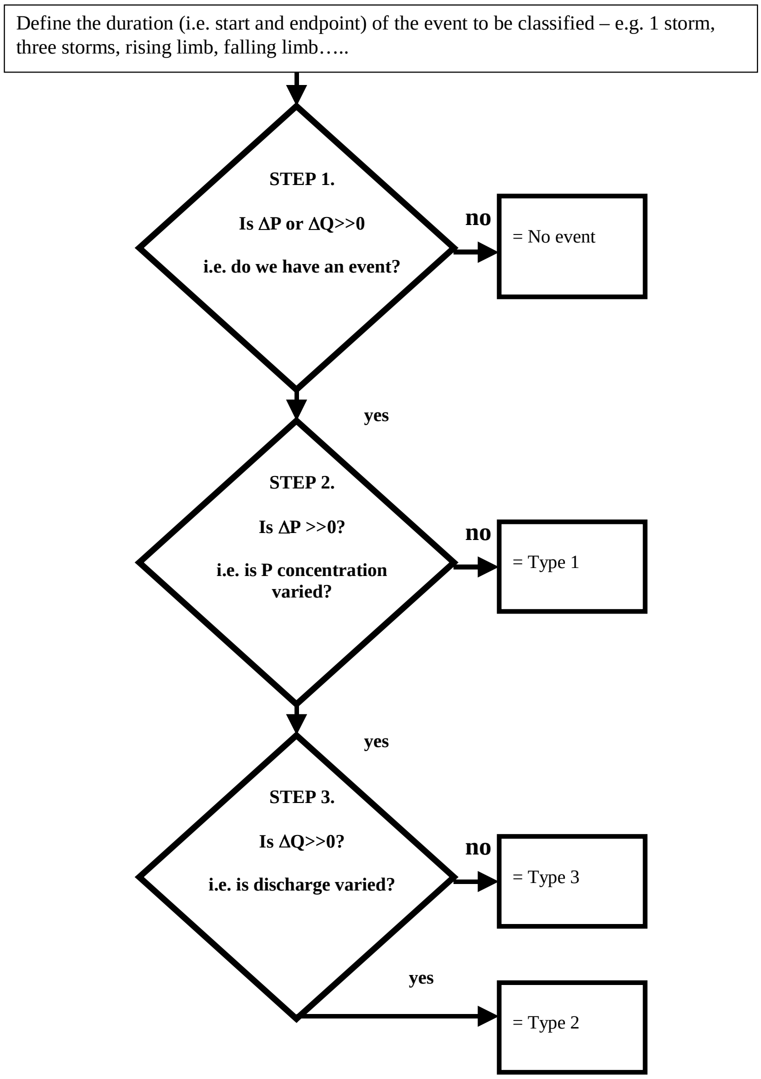

Fig. 1. *Proposed system for a functional type classification of phosphorus concentration–discharge relationships*

in England and Wales (MAFF, 1994). The lysimeters were exposed to natural rainfall and environmental conditions and water draining under gravity was collected in 25 L vessels in an underground chamber (Turner and Haygarth, 2000). There were three soil types and four replicate lysimeters of each, being; (1) a clay loam (USDA Dystrochrepts), (2) a sandy-loam (USDA Hapludalfs) and (3) a sand (USDA Udipsamments). The temporal trend, based on seven-day cumulative Q over a winter field capacity season, from 2nd December 1997 until 19th May 1998, was studied. The Dystrochrepts soil was also analysed more frequently, using samples gathered daily, during the period 18th February–4th March 1997.

1.8 hectare size overland/interflow plots. This experiment used a 1.8 hectare paddock as part of a 120 ha farm on which approximately 350 dairy cows graze all year round at Darnum, in West Gippsland, Victoria, Australia (38 10' S, 146 03' E). The soil was a fine sandy loam A horizon overlaying a light to medium clay at approximately 75 cm (USDA Haplustults). The pasture was predominantly perennial ryegrass and white clover (*Trifolium repens* L.) and received 60, 80, 110 and 110 kg P ha^{-1} annually from 1993 to 1996. The experimental area drains to a natural depression where a culvert conveys the water away. Overland flow plus interflow to 7.5 cm were sampled by a diversion wall, buried 7.5 cm into the soil. Water sampling was discharge-integrated to maximise sampling frequency at higher Q for 34 events >0.027 mm (runoff) between 1994 and 1996.

Den Brook headwater catchment. This 48 ha catchment was

Table 2. Description of the soils and hydrological circumstances examined in this study

Soil type (USDA system)	*Location*	*Hydrological circumstances and sampling*	*Management*	*Annual rainfall (mm)*	*Soil Olsen P (mg kg^{-1})*
Dystrochrepts	Institute of Grassland and Environmental Research, North Wyke, Devon, UK	80 cm diameter × 135 cm, deep monolith lysimeter: percolate at 135 cm	Cut grassland, (*Lolium perenne* L.), 25 kg P ha^{-1} per year as fertilizer, 4 replicates	1100	24
Hapludalfs	Institute of Grassland and Environmental Research, North Wyke, Devon, UK	80 cm diameter ×135 cm, deep monolith lysimeter: percolate at 135 cm	Cut grassland, (*Lolium perenne* L.), 25 kg P ha^{-1} per year as fertilizer, 4 replicates	1100	46
Udipsamments	Institute of Grassland and Environmental Research, North Wyke, Devon, UK	80 cm diameter ×135 cm, deep monolith lysimeter: percolate at 135 cm	Cut grassland, (*Lolium perenne* L.), 25 kg P ha^{-1} per year as fertilizer, 4 replicates	1100	75
Haplustults	Darnum, Victoria, Australia	1.8 ha paddock, overland flow plus interflow to 7.5 cm	Grazed pasture, *Lolium perenne* L. and *Trifolium repens* L., 60, 80, 110 and 110 kg P ha^{-1} annually from 1993 to 1996	1000	40
Dystrochrepts	Drewston, Devon, UK	22 ha first order headwater catchment, 639 mm runoff	Grazed pasture, *Lolium perenne* mixture of beef cattle and sheep	1311	49
Typic haplaquepts	Den Brook, Devon, UK	48 ha first order headwater catchmentl, 610 mm runoff	Grazed pasture, *Lolium perenne* mixture of cows, beef cattle and sheep	1011	54

characterised by a slowly permeable seasonally waterlogged clay soil (USDA Typic Haplaquept) and had an extensive network of agricultural tile drains under the surface. The catchment was managed predominately as mixed grassland with some beef cattle, sheep and a dairy herd, as well as approximately 1 ha of maize, harvested in the autumn. The median Olsen P value for the whole catchment was 54 mg kg^{-1} (0–7.5 cm). There was also a hard standing area for cattle within the catchment that drained, intermittently, polluted farmyard runoff directly into the stream. The sward was dominated by perennial ryegrass and received inorganic fertiliser N, P and K plus manure and excretal returns consistent with recommended practice (MAFF, 1994). Annual average rainfall for the period Dec 2001–Nov 2002 was 1011 mm with 610 mm total runoff determined at the flume at the outlet (located at UK national mapping grid reference NGR SX 677 998). Water samples were auto-collected in proportion to the flow and transferred to the laboratory for analysis within 24 hours of sampling.

Drewston headwater catchment. This 22 ha catchment was characterised by a well drained fine loamy soil (USDA Dystrochrept) and was approximately 10 miles from the Den Brook catchment, thereby being subjected to a broadly similar and comparable hydro-climatic condition. The catchment was managed predominately as mixed grassland with some beef cattle and sheep, as well as having woodland surrounding the stream in the lower part of the catchment. The median Olsen P value for the whole catchment was 49 mg kg^{-1} (0–7.5 cm). The sward was dominated by perennial ryegrass and received inorganic fertiliser N, P and K plus manure and excretal returns consistent with recommended practice (MAFF, 1994). Annual average rainfall in the period Dec 2001–Nov 2002 was 1311 mm with 639 mm total runoff determined at the flume outlet (UK national mapping grid reference NGR SX 726 878). Water samples were auto-collected in proportion to the flow and transferred to the laboratory for analysis within 24 hours of sampling.

How understanding C_p–Q relationships can contribute to new understandings for phosphorus transfer

Pionke *et al.* (1996) have demonstrated previously the importance of 'events' and proposed a system of classifying nutrient export by separating hydrograph Q conditions in relation to 'base flow', 'elevated base flow', 'storm flow' and 'unclassified flow'. This classification system was based on Q and did not account for differences in C_p. In contrast, the approach taken here is able to describe all types of C_p–Q relationships that emerge from the data sets. In Figs. 2-6, examples are presented as illustrations.

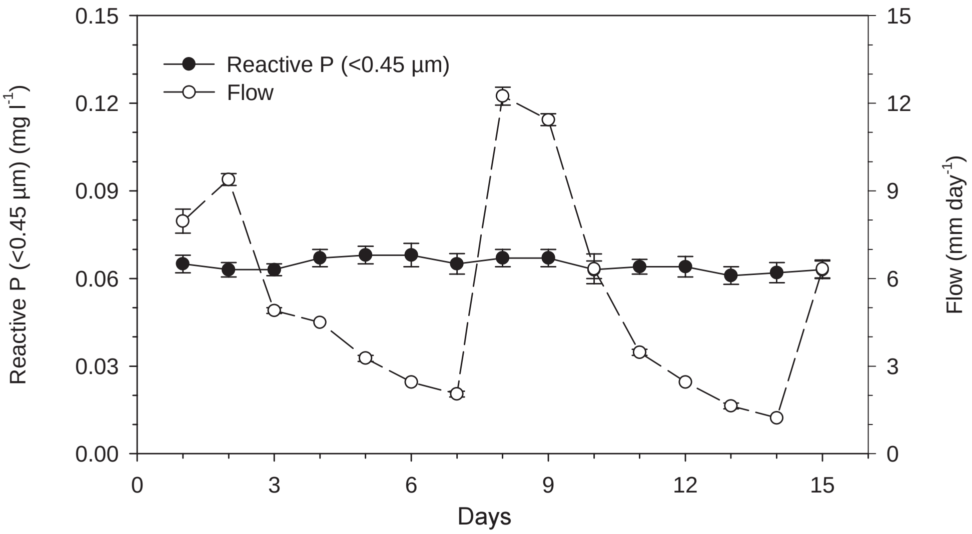

Fig. 2. *Type 1 response in monolith lysimeters at daily resolution for two weeks, (one soil type): The temporal trend in* $RP_{<0.45\ mm}$ *concentration in leachate and discharge from a Dystrochrepts soil under a cut grassland monolith lysimeters in Devon, UK. Data are from samples gathered daily, during the period 18th February – 4th March 1997, vertical bars represent standard errors of n = 4 replicate lysimeters).*

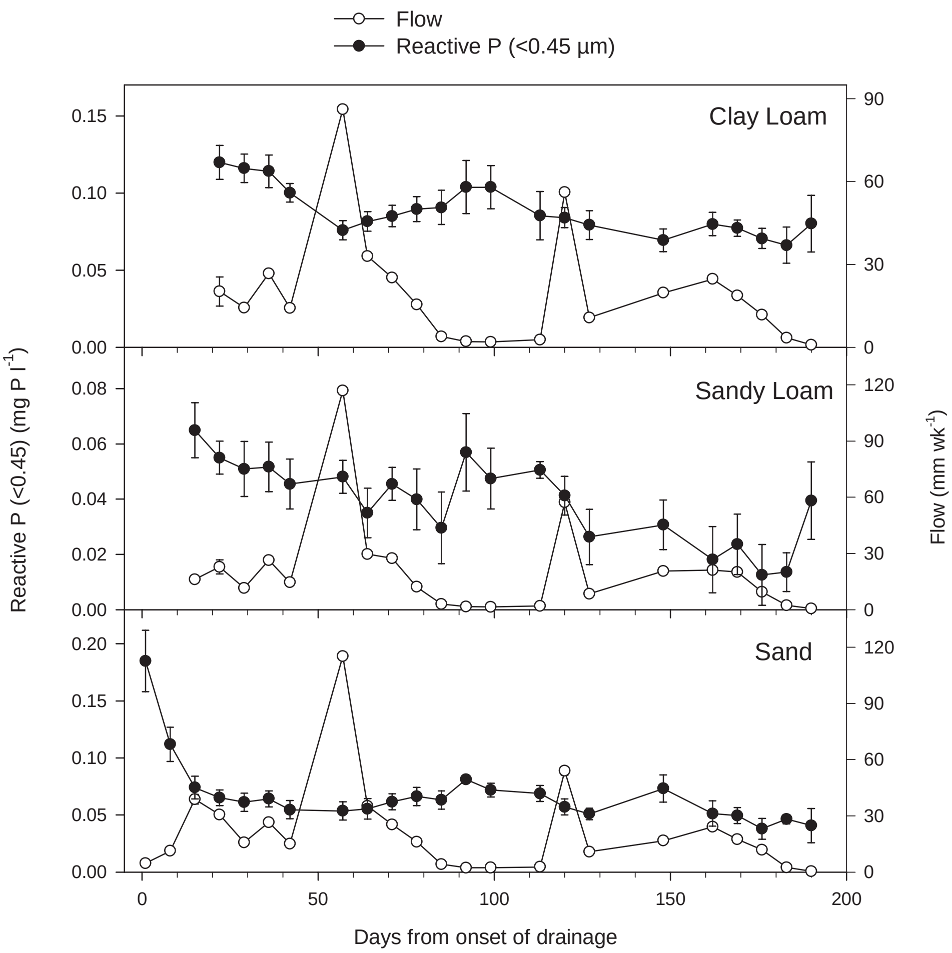

Fig. 3. *Type 1 response in monolith lysimeters, at weekly resolution for a drainage season (3 soil types): The temporal trend in* $RP_{<0.45\ mm}$ *concentration in leachate and discharge from three contrasting soil types in monolith lysimeters under cut grassland in Devon, UK. The temporal trend is based on a 7-day cumulative discharge over a winter field capacity season, from 2nd December 1997 until 19th May 1998, vertical bars represent standard errors of n = 4 replicate lysimeters).*

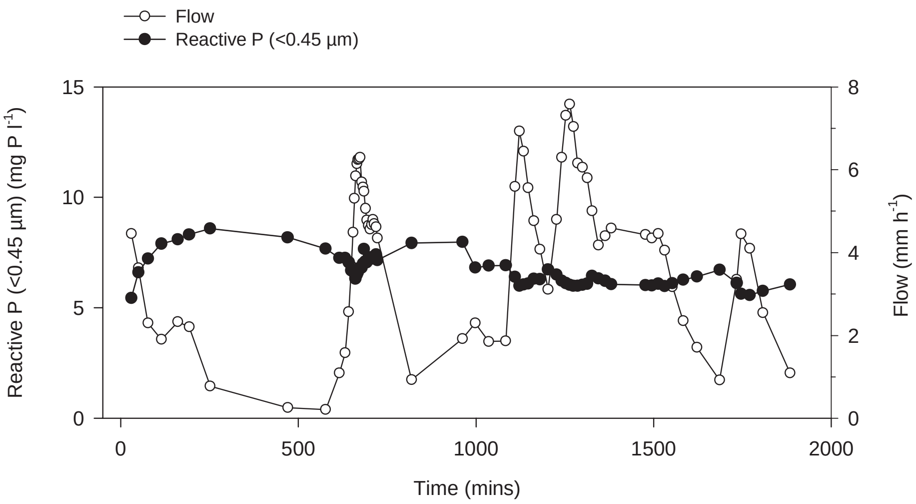

Fig. 4. *Type 1 response in overland flow from a small paddock from 1.8 ha overland flow plus interflow plots from Darnum in Victoria, Australia. These data are from the longest continuous event of >0.027 mm at this site. This data was collected on a minute by minute scale on 6–7 Nov 1994.*

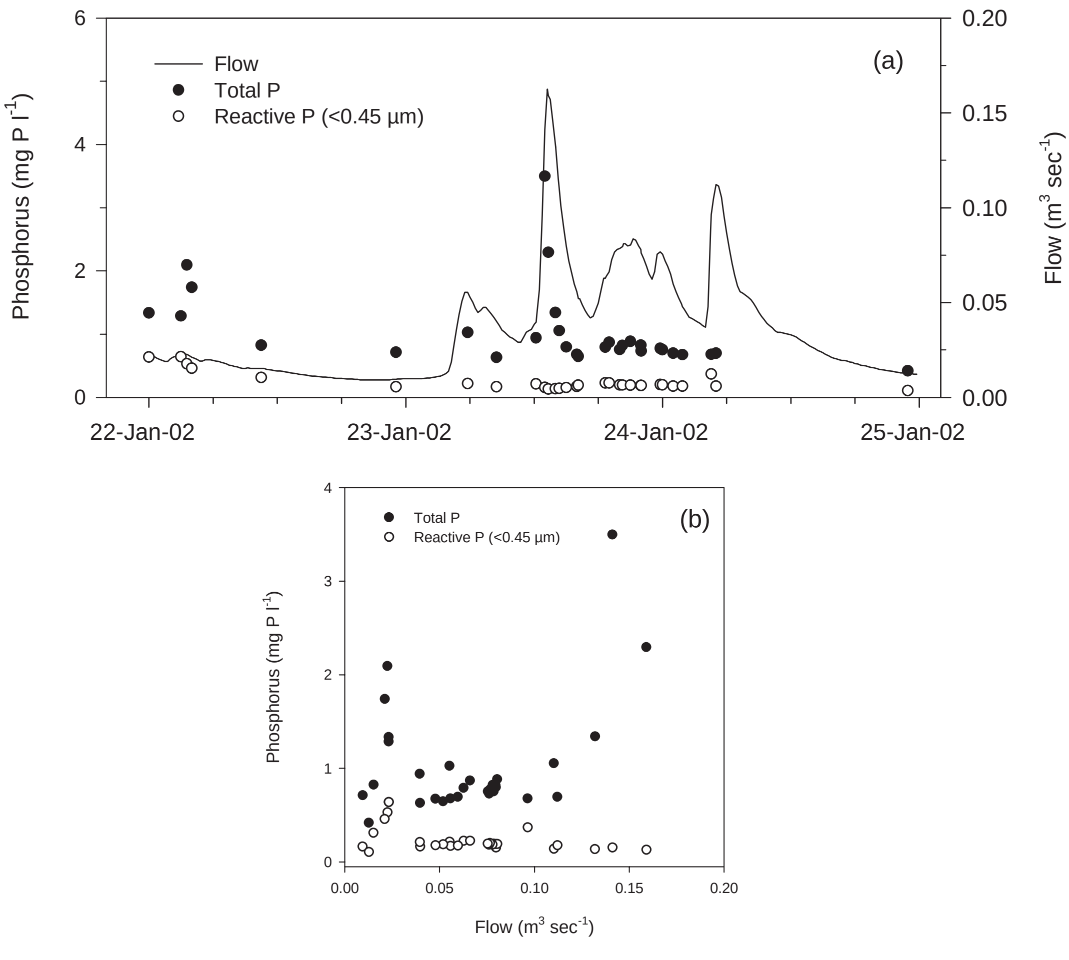

Fig. 5. *Different phosphorus forms give different functional type responses: Type 1 and 2 responses in one-headwater catchment for different P forms. (a)Temporal trends in $RP_{<0.45\,mm}$ (Type 1) and TP concentration (Type 2) and discharge on 23rd January 2002 in the Den Brook catchment. (b) Scatter plot of the resulting relationship between C_p and Q.*

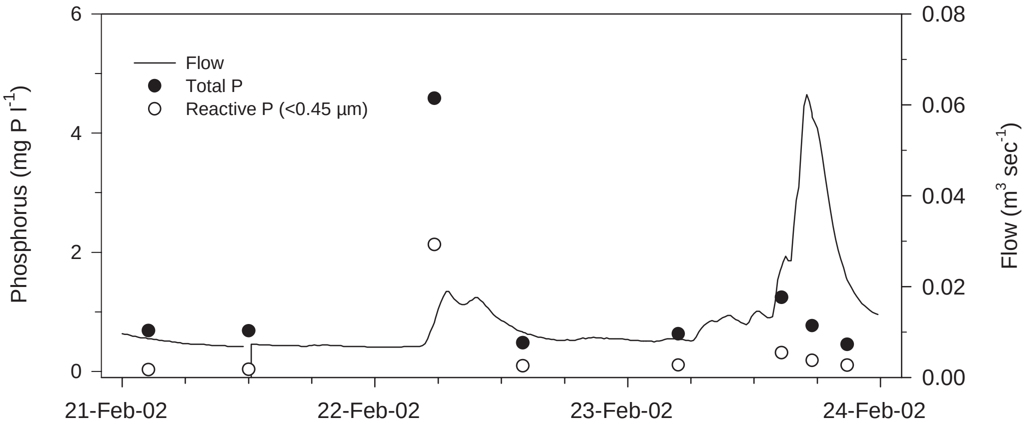

Fig. 6. *Type 3 response in one-headwater catchment: Temporal trends in a) $RP_{<0.45\ mm}$ and b) TP concentration and discharge on 21-24 February 2002 in the Den Brook catchment, following wash down of animal housing area into the stream.*

Example of Type 1 circumstances and the effect of sample frequency. Type 1 transfers (akin to the term 'level 1' that was first used by Haygarth and Jarvis (1999) and Haygarth *et al.* (2000b)) are similar to 'systematic' transfers described by Nash *et al.* (2001) and 'underlying agricultural transfers' (Haygarth *et al*., 2000b), associated with 'base flow' (1996). Type 1 C_p–Q relationships exemplify a strongly damped 'flat' or 'smooth' P breakthrough, in relation to a relatively varied response of Q, suggesting that matrix type Qs are dominant, where water, P and soil have become reasonably well mixed. In these circumstances, Q limits P transfer. Type 1 responses were most common from small scale observations (i.e., monolith lysimeters).

Time series plots of $RP_{<0.45\ \mu m}$ breakthrough concentrations and Q for the Dystrochrepts monoliths are shown in Fig. 2, using samples gathered daily during the period 18th February–4th March 1997 (Fig. 2 – clay loam) and collected weekly for the entire hydrological drainage period 1997–1998 (Fig. 3 – clay loam, sandy loam and sand). Double Fourier models (Genstat 5 Committee, 1993) were fitted to both Q and $RP_{<0.45\mu m}$ concentration. For the clay loam, the maximum amplitudes of the Qs were 78.8% (Fig. 2, daily sample frequency) and 99.5% (Fig. 3 – weekly sample frequency), whereas for $RP_{<0.45\ \mu m}$ concentration they were 3.7% (Fig. 2 - daily) and 45.9% (Fig. 3 – weekly). In the first example (Fig. 2 – daily), the maximum amplitude of Q was 21 times greater than the maximum amplitude of $RP_{<0.45\ \mu m}$ and in the second longer sample period (Fig. 3, weekly), it was 2.7 times greater than that of the $RP_{<0.45\ \mu m}$. Figure 3 also shows weekly sample data from the other two monolith soils (Hapludalfs and Udipsamments) plotted in a similar manner. In these hydrographs, the maximum amplitudes of the Qs were larger than those for $RP_{<0.45\ \mu m}$ concentrations in the time series. A similar Type 1 classification is shown for the 1.8 ha size overland Q plots from Australia (Haplustults, Fig. 4), although in this example there is additional finer structure to the hysteresis. At the beginning of the time series values are clearly recovering on the falling limb of the first runoff event and the pattern is repeated throughout successive Q peaks. All these data exhibit a Type 1 classification.

Example - Type 1 and 2 circumstances and the effect of phosphorus forms. Different P forms can also result in different functional type behaviour. Figure 5 is an example from Den Brook from January 2002, where, in the main storm peak, temporal trends in $RP_{<0.45\ \mu m}$ are Type 1 but total P forms gave a Type 2 response. This probably reflects different processes of mobilisation of different forms of P. Where P forms are filtered, they predominantly reflect solubilisation of P that can be relatively easily mixed in matrix flow paths of the soil. In contrast, TP includes P forms that are not soluble and thus reflects physical detachment of colloids and particles with P attached, responding to the physical energy of the rainfall (Haygarth and Jarvis, 1997). Interestingly, before and after the main storm peak where Q is lower, TP actually exhibits a Type 1 response, illustrating the importance of hydrological thresholds in determining the switch in hydrological energy (Haygarth *et al*., 2000a). Figure 5b shows the scatter plot of the relationship between C_p and Q is more widely distributed than that for $RP_{<0.45\ \mu m}$ which, being more akin to Type 1, is less responsive to Q.

Example of Type 3 circumstances and farm management. An example of a Type 3 response from the Den Brook catchment occurred on 21–24th February 2002, following leakage of the slurry storage pit into the drain that feeds the stream (Fig. 6). This type of event is clearly source-dominated.

Benefits of a temporal approach to studying phosphorus transfer

This simple rationalisation of C_p–Q relationships emphasises the importance of a *temporal* approach characterising circumstances of P transfer. With the exception of a few studies cited earlier, the overall trend within the P transfer cognoscenti has been to focus on *static/spatial* factors. Events are a source of important information for helping the understanding of patterns and processes and clearly C_p and Q are the central components of these. Although factors such as soil P status are important in the long term (Heckrath *et al*., 1995), not studying mechanisms in a dynamic and temporal framework may result in loss of valuable information and potential to understand extremes of land management and antecedent conditions. Clearly Type 1 scenarios generate smaller loads and may need less (short term) mitigation requirement than Types 2 and 3.

Several simple but important rules that can promote progress on understanding of P transfer have emerged from this work:

- Sample frequency is important and can potentially affect the interpretation of C_p–Q relationships and the functional type of an 'event'. Higher sample frequencies could reduce potential uncertainties and so should be a priority.
- In Type 1 conditions, studying soil P does not lead to an understanding of short term P transfer dynamics. Thus, in the short term, static agronomic measures such as Olsen P do not explain the P load and the associated mechanisms.
- Phosphorus form affects C_p–Q relationships. In the same catchment in the same event, soluble RP exemplified Type 1 whereas TP (that included particles and colloids) exemplified Type 2.
- A large P source affects C_p–Q relationships. A Type 3 response was noted where a slurry source leaked directly to the stream.
- Scale affects C_p–Q relationships. Type 1 responses seem to be more common in small scale studies, e.g. in monolith lysimeters, presumably because, at this scale, monoliths are relatively well homogenised. However, it is important to acknowledge that had by-pass flow occurred, a different type of response may have been observed. Nonetheless, this casts doubts on the validity of extrapolating from lysimeters to catchments.

Future challenges

This simple framework provides a basis for development of a more complex and quantitative classification of C_p–Q relationships. The practical benefit of this approach is that it could contribute to a dynamic modelling framework for helping understand P transfer and delivery from slope to stream and an attemptis now being made to do this. Here, examples from various new data sources have been selected but future improvements could be made from development of a quantitative means to classify 'Type' that takes into account any non-linearity that can exist between C_p and Q. This is because the main limitation in the classification is that it is qualitative and that subjective judgment is required in interpretation of C_p–Q relationships. Another priority for consideration is that, as different processes can lead to the same C_p–Q response, they are, in practice, difficult to separate (there are at least three mechanistic explanations for a Type 2 response): this is the problem of geomorphological equifinality as identified previously by Beven (1996). Therefore, there is also a need to develop a system to separate different types of responses, with a sub-categorisation to explore finer structure of within-storm hysteresis, to determine whether C_p peaks occurred before or after the Q peak for Type 2 conditions. This could build on the precedents established in the sediment literature that have earmarked the importance of different conditions for transport versus supply-limited events (e.g. Williams, 1989; Wood, 1977).

This paper has identified the importance of *temporal* approaches to P transfer, to help guide future understanding of mechanisms that determine loads (load = C_p.Q). Since P loads are the basis for export coefficients that are, in turn, used to 'calibrate' spatial/static models (Heathwaite *et al*., 2003; Johnes and Butterfield, 2002; Lemunyon and Gilbert, 1993) that inform policy decisions, C_p–Q dynamics are of fundamental importance. It is intended that this paper serves as a stimulant and commentary on current approaches to the P transfer issue and highlights the need for future studies to adopt dynamic approaches. Future challenges are to develop quantitative model frameworks that help pinpoint *when, where* and *why* these different situations occur.

In a wider context, the classification scheme is dependent on the resolution, duration and overall quality of the input data. As contemporary publications have shown (Kirchner *et al*., 2000; Kirchner *et al*., 2001; Kirchner *et al*., 2004), fine resolution monitoring may reveal additional patterns of complexity. Events therefore may not be linked only or directly to flow and intermittent farm managements, but due to a wide distribution of water and P through residence times. This fractal response has been shown to occur in similar ways across a large variety of scales. Therefore, the only true understandings in P hydrochemistry will come about by more high resolution dynamic observations across scales.

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